



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

International Patent Classification 6:

H01M 4/62, 4/50

A1

(11) International Publication Number:

WO 00/11739

(43) International Publication Date:

2 March 2000 (02.03.00)

(21) International Application Number: PCT/US98/08825

(22) International Filing Date: 1 May 1998 (01.05.98)

(71) Applicant (for all designated States except US): EVEREADY BATTERY COMPANY, INC. [US/US]; 25225 Detroit Road, Westlake, OH 44145 (US).

(71)(72) Applicant and Inventor: URRY, Lewis, E. [US/US]; 36263 Butternut Ridge Road, Elyria, OH 44039 (US).

(74) Agents: WELSH, Robert, W. et al.; Eveready Battery Company, Inc., 25225 Detroit Road, Westlake, OH 44145 (US).

(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GR, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published

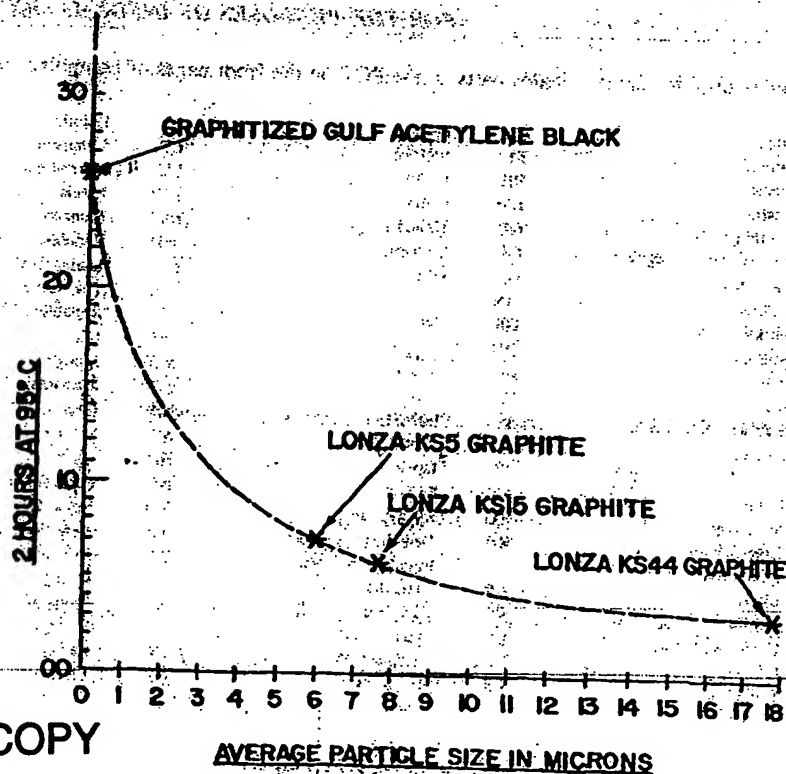
With international search report.

(54) Title: HEAT TREATED FINE CARBON FOR ALKALINE MANGANESE CATHODES

## (57) Abstract

Heat treated fine carbon has small particle size and can be used as the electroconductive element in cathodes of electrochemical cells to reduce the volume taken up by non-active materials by increasing contact between the active material and the electroconductive element.

**EFFECT OF PARTICLE SIZE ON OXYDATION RESISTANCE  
GRAPHITE VS. GRAPHITIZED GULF ACETYLENE BLACK**



BEST AVAILABLE COPY

AVERAGE PARTICLE SIZE IN MICRONS

## 5 HEAT TREATED FINE CARBON FOR ALKALINE MANGANESE CATHODES

## BACKGROUND OF THE INVENTION

10 The present invention generally relates to a heat treated fine carbon as a conductor in a cathode mixture of electrochemical cells.

Conventionally, the positive electrode of alkaline manganese batteries comprises mixtures of electrolytic manganese dioxide (EMD) as the positive electrode active material, and carbon as the electroconductive material. The electroconductive material is necessary because the specific conductivity of manganese dioxide alone is  
15 extremely low. When electroconductive carbon materials are used in large quantities, the quantity of manganese dioxide that can be used in a battery's fixed internal volume is decreased. Consequently, the discharge capacity density of the battery is decreased to a very great extent. On the other hand, when an insufficient amount of the  
20 electroconductive carbon is used, there is decreased contact between the manganese dioxide and the carbon. This results in a decreased electron conduction network, and the overall utilization rate of the manganese dioxide in the electrode is thereby decreased. By using a finer conductor material, especially compared to the size of the manganese dioxide, a lesser amount of conductor material is needed to get an  
25 adequate electron matrix. The finer particle-size particles reduce the volume percent solids without reducing the input per volume of active materials, or increases the input of active materials per unit volume of the solids packing. The advantages of using a very fine conductor material are well known, but difficult to achieve.

5

## SUMMARY OF THE INVENTION

This invention is an electrochemical cell having an anode, a cathode, and an electrolyte, wherein the cathode comprises a heat-treated fine carbon as an electronic  
10 conductor.

In yet another aspect, this invention is an alkaline cell having a cathode comprising a conductor at less than 6 volume percent of the positive electrode.

In still another aspect, this invention is an alkaline cell having a cathode mixture comprising fine carbon having a high oxidation resistance of less than 30  
15 milliliters  $K_2Cr_2O_7$ /gram, as determined by a potassium dichromate digestion test described herein.

The alkaline cell of this invention has a cathode that has good oxidation resistance, and good electrochemical performance at a low volume percent of the positive electrode.

20

## BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a graph of effect of particle size on oxidation resistance of heat treated fine carbon vs. graphites.

25 Figure 2 is a graph comparing three D-size cells containing different types of conductor materials.

## DESCRIPTION OF THE INVENTION

30 According to the present invention, a mixture comprising a heat treated fine carbon with manganese dioxide provides an improved positive electrode for alkaline cells. The heat treated fine carbon of this invention can be produced using a fine carbon material such as acetylene black, that is treated, for example, at a temperature

5 Fe++ to milliliters  $\text{Cr}_2\text{O}_7^{2-}$ . The normality factor is used to calculate the number of milliliters of potassium dichromate solution consumed per gram of sample in a given time.

The oxidation resistance is expressed as the number of milliliters of  $\text{K}_2\text{Cr}_2\text{O}_7$  solution consumed per gram of sample. The lower the value, the greater its resistance to oxidation. The heat treated fine carbon according to this invention is 4.5 times more resistant to oxidation compared to the starting material.

#### 15 RESISTANCE TO OXIDATION

Carbon Material	Oxidation resistance (milliliters of $\text{K}_2\text{Cr}_2\text{O}_7$ consumed per gram of sample)
Chevron Acetylene Black - conventional	118.3 mL/gram
Chevron Acetylene Black - heat treated	25.83 mL/gram

#### DETAILED DESCRIPTION OF DRAWINGS

20 Figure 1 is a graph of effect of particle size on oxidation resistance of heat treated fine carbon vs. graphites. As can be seen by this graph, the carbon after graphitization had the same oxidation resistance as graphite per unit surface area or particle size.

Figure 2 is a graph comparing three D-size cells containing different types of conductor materials. Cell 1 has heat treated acetylene black as a conductor at 5.8 volume percent; cell 2 has graphite as a conductor at 13.7 volume percent; and cell 3 has combined graphite and conventional acetylene black.

BEST AVAILABLE COPY

5

Although the present invention has been fully described by way of example with reference to the accompanying drawings, it is to be noted here that various changes and modifications will be apparent to those skilled in the art. Therefore, unless otherwise such changes and modifications depart from the scope of the present invention, they should be construed as being included therein.

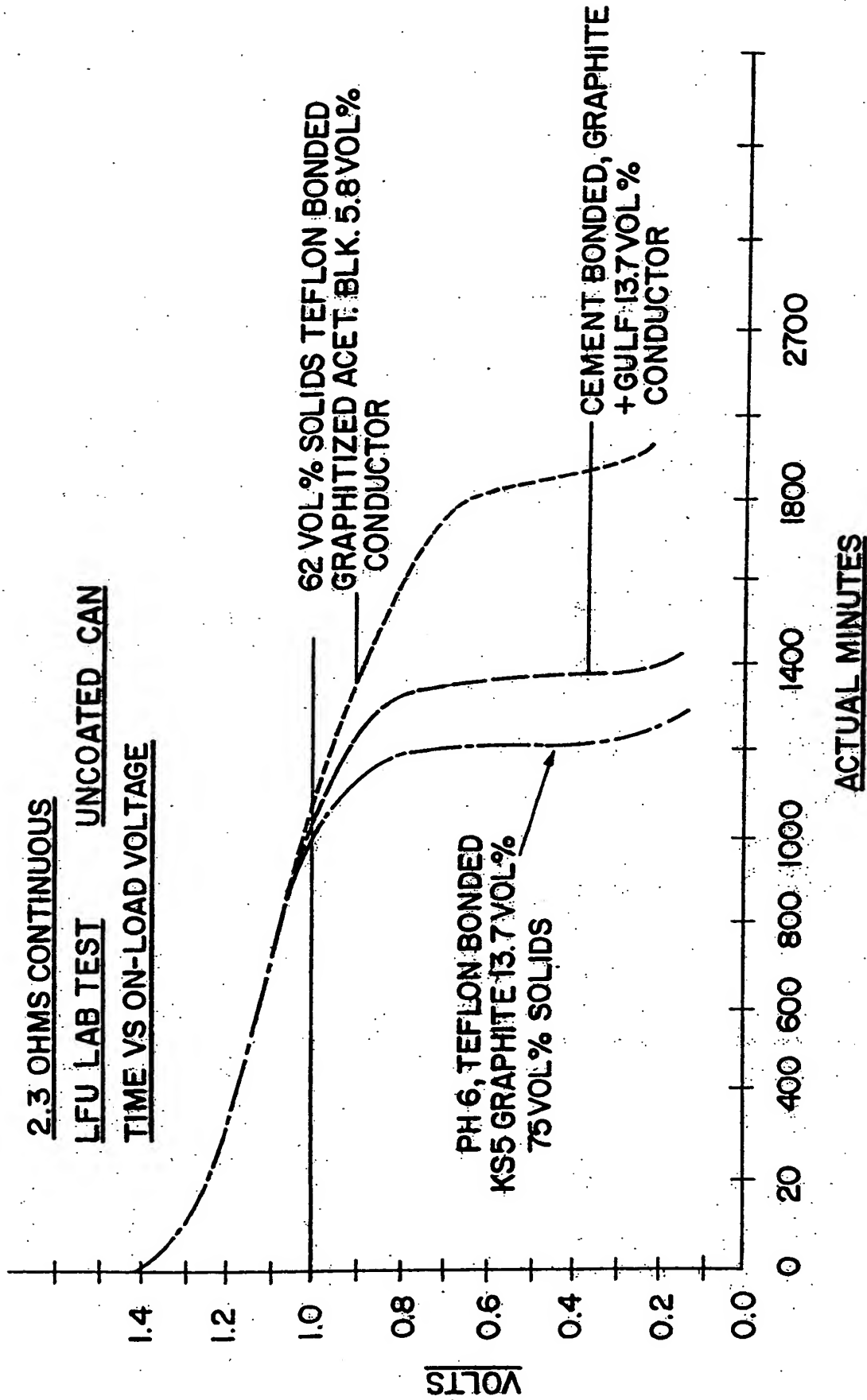
BEST AVAILABLE COPY

- 5 (11) The electrochemical cell of claim 2, wherein the conductor has an average particle size between about 50 Angstroms to about 200 Angstroms.

12. The electrochemical cell according to claim 2, wherein the conductor has an oxidation resistance of less than 30 milliliters 0.1 N potassium dichromate digested per gram of carbon, as measured by a potassium dichromate test.

- 10 13. An electrochemical cell having an anode, a cathode, and an electrolyte, said cathode comprising a conductor having an oxidation resistance of less than 30 milliliters 0.1 N potassium dichromate digested per gram of carbon, as measured by a potassium dichromate test.

BEST AVAILABLE COPY

*Fig. 2*

BEST AVAILABLE COPY

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 98/08825

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0322806	A	05-07-1989	JP 1176663 A	13-07-1989
			US 5017445 A	21-05-1991

BEST AVAILABLE COPY